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# Propagating Polymerization Fronts

## Final Report

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## 2. Objectives

We have focused on three aspects of the materials that can be produced in a front:

- 1) Determine the variables that affect the conversion and molecular weight distribution for polymer formed in fronts in liquid monomers and in solid monomers.
- 2) Study controlled morphologies in binary fronts.
- 3) Develop new methods to produce functionally gradient materials.
- 4) Determine the properties of frontally cured epoxy resins.

## 3. Status of Effort

We have determined the factors that affect front velocity, conversion and molecular in frontal polymerization with liquid monomers and made some progress with solid monomer systems. We developed the first binary system, consisting of acrylate polymerization via a free-radical mechanism and the curing of an epoxy resin. A full IPN is produced. We also prepared the first frontal polymer dispersed liquid crystal (PDLC) material. We developed a method to suppress convective instabilities via tube rotation and have determined the critical conditions affecting ascending front stability with respect to natural convection. We have studied the frontal curing of DEGEBA epoxy resin. We developed new method to prepare functionally gradient materials.

## 4. Accomplishments/New Findings

### *Factors Affecting Frontal Polymerization*

We have analyzed fractionated samples of poly(methacrylic acid) produced in a propagating front for the amount of anhydride that formed and determined that a large percentage of acid groups exist as anhydrides (> 20%). By analyzing the samples after cleavage, we found that the molecular weight dropped significantly (from  $M_n = 1.4 \times 10^5$  to  $M_n = 1.0 \times 10^4$ ). We conclude that the high molecular weights observed previously were the result of intermolecular anhydride formation. Poly(butyl acrylate), which can not form anhydride bonds, produced in fronts had broad ( $M_w/M_n = 1.7 - 2.0$ ) but unimodal molecular weight distributions with  $M_w < 10^5$ ). The average molecular weight decreased with increasing initiator concentrations.

Now these fronts have also been observed in solid monomers such as acrylamide, zinc dimethacrylate, and a mixture of both monomers. Some of the initiators used in these solid-monomer polymerization fronts are benzoyl peroxide, azobisisobutyronitrile (AIBN), and potassium persulfate.

The effect of packing force and particle size of the monomer and initiator on propagation velocity has been studied in the acrylamide-potassium persulfate system. It was found that applied force had an effect on the velocity of the front while particle size of the monomer and initiator produced interesting trends in velocity. Obtaining reproducible results was very difficult.

We have studied propagating fronts using a solid monomer (Acrylamide) with a solid filler ( $\text{BaCO}_3$ ) and an initiator (Lauroyl Peroxide). We have observed periodic, uniform banding of reacted sample in this system. Possible reasons that could explain the occurrence of the banding are phase separation processes, filtration of the melted reactants, and pressure fluctuations. While seeking to discover the parameters that cause a front to form the banding and to ascertain plausible explanations for the phenomenon, we have also obtained the velocity of fronts using different concentrations and different particle sizes.

**Relevance:** Frontal polymerization could be a more efficient method to produce polymers, with less waste produced. Understanding the factors affecting the process and the product produced is necessary to evaluate its prospects.

### *Development of Pressure Reactor*

Experiments were performed in a custom-built reactor of our design that allowed isobaric and isothermal conditions. We found that the front velocity was a function of the applied pressure, even at low values of less than 30 atm. As the pressure is increased, the velocities decrease, exactly opposite the behavior observed by Chechilio and Enikolopyan at high pressures! At the low pressures we employ, we are not affecting the rate constants of polymerization but suppressing bubbles.

There are three sources of bubbles. All the thermal initiators we have investigated (except sodium persulfate, which is insoluble in most monomers) produce volatile by-products, such as  $\text{CO}_2$ , methane and acetone. It is an inherent problem with all commercially available peroxide or nitrile initiators.

Another source of bubbles is dissolved gas and water in the monomer. Gases can be removed under vacuum but water is extremely difficult to remove from methacrylic acid and TGDMA. Less than 1 mg of water will result in  $2 \text{ cm}^3$  of water vapor at the front temperature of  $200^\circ\text{C}$  and 1 atm of pressure. The only certain solution to all three sources is to perform reactions under pressure.

Bubbles can increase the velocity of fronts in standard closed test tubes initially at ambient pressure by as much as 30% compared to fronts free of bubbles under high pressure. The expansion of bubbles is part of the velocity by forcing unreacted monomer up and around the cooling polymer plug that is contracting; poly(methacrylic acid) is about 25% more dense than its monomer. This means that the pressure increases during the reaction because the tube is sealed, except for leakage around the initial polymer plug.

For pressure (up to 50 atm) experiments the reaction vessel was placed in an all-glass pressurized chamber and oriented in such a manner that the sealed end was at the top and the open end in the downward direction. A movable air-tight piston at the open end contained the reactants. An increase of pressure in the pressure chamber caused the piston to move inwards in the reaction tube and vice versa to compensate for any resulting pressure difference between the chamber and the reaction tube. A subminiature thermocouple probe (Omega TMQSS-0.020(G)-12") passed through the piston and was formed into a spiral parallel to the front surface for temperature profile measurements.

The pressurized chamber was submerged in a large temperature-controlled water bath equipped with an oblong window. A motorized video camera monitored the downward propagating front in the reaction chamber. A mass flow controller (Omega FMG 7201) maintained a  $100 \pm 1 \text{ cm}^3\text{min}^{-1}$  nitrogen flow upwards along the sides of the reaction vessel to prevent an increase in temperature in the pressure chamber. The nitrogen was equilibrated to the water bath temperature via a copper coil before entering the chamber.

### *Frontal Curing of Epoxy Resins*

We determined that some amine curing agents can work with DEGEBA epoxy resin to support frontal curing. We found that a product with 90% of the mechanical properties of a batch cured sample could be achieved without an oven.

**Relevance** Frontal curing of epoxies would allow curing of large composites without the use of an autoclave.

### **Frontal Polymerization in Solution**

Frontal polymerization of several reactive monomers can be performed in high boiling point solvents. Acrylamide polymerization will propagate in water (with some vaporization of water), in dimethyl sulfoxide (DMSO) and in dimethyl formamide (DMF) with several initiators, including sodium persulfate, potassium persulfate, ammonium persulfate, and benzoyl peroxide. Several other monomers also work in these solvents, including acrylic acid, sodium methacrylate and zinc dimethacrylate. For a monomer to support frontal polymerization in a solvent, the enthalpy of the reaction must be sufficiently high that dilution does not lower the front temperature below a front-sustaining value.

Interestingly, no gas bubbles are observed with acrylamide/persulfate in DMSO, the only system we have found with this feature at ambient pressure. (The persulfates do not produce volatile side products.) Bubbles can interfere with front velocity measurements and can affect the stability of the front.

Because of the density difference between the polymer and monomer, a descending front can be subject to double-diffusive and/or Taylor instabilities that manifest themselves as descending "fingers". Fronts of acrylamide in DMSO (1:1) do not exhibit extensive fingering because the polyacrylamide gels. However, acrylic acid, which does not gel in DMSO, exhibits rampant fingering and will not propagate without the addition of a few percent of bisacrylamide (a difunctional monomer), which produces a crosslinked and solid product. The same is true for acrylamide in DMF. To suppress fingering, which can affect the front velocity, all experiments were performed with 1 % (w/w) of bisacrylamide, with respect to the acrylamide. With DMSO as the solvent, a rubbery polymer was produced.

We measured the temperature profile of the front with 1:1 (w/v) acrylamide. The temperature increased 165 °C over 3 mm. Taking the  $\Delta H$  of polymerization to be 570 kJ/mol and the heat capacity of acrylamide/DMSO solution to be 2 J/mL, we estimate conversion to be 60%. In fronts with powdered acrylamide, Pojman et al. reported conversion from 60% to 90%, depending on the amount of initiator.

We determined the velocity as a function of persulfate concentration for fixed acrylamide concentration. The dependence on the initiator concentration is not a power function, as has been observed for frontal polymerization with pure monomers. Secondly, the front velocities are several times greater than fronts with neat acrylates but comparable to fronts with powdered acrylamide.

Unlike neat monomer systems, the concentration of monomer can be varied to change the propagation velocity. Below 0.4 g/mL, no front would propagate.

The ability to perform frontal polymerization with many different monomers in several high boiling point solvents greatly increases the systems that can be studied and types of materials that can be prepared.

### **Binary Frontal Polymerization**

We report a new method of simultaneous interpenetrating polymer network (SIN) formation using a thermal propagating front of two independent and noninterfering polymerization mechanisms. The system consists of free-radical crosslinking of triethylene glycol dimethacrylate (TGDMA) and the amine/ $\text{BCl}_3$ •amine curing of diglycidyl ether of bisphenol A (DGEBA). The front velocity dependence on the percentage of each monomer shows a minimum at 45% TGDMA. Temperature profile measurements indicate that a single reaction front propagates.

We tested the front velocity dependence on relative amounts of the two polymerization systems. It was shown to decrease with an increase in the relative amount of the free radical monomer up to fifty percent after which the velocity increased (Figure 2). The velocity of the front for a given monomer system has been shown to increase with an increase in concentration of the activating species. The convex nature of the velocity versus percentage monomer curve is due to a competition between dilution of one polymerization system and concentration of the other polymerization system. Whereas the amount of activating species was kept constant relative to the respective monomer, the actual concentration in moles per liter changed significantly as the relative amounts of the polymerization systems changed. Due to the constant change in moles per liter of all reactants and the nonlinearity of the rate equations, we concluded that there will always be a minimum in this velocity versus percentage monomer curve.

The non-monotonic nature of the velocity dependence along with the temperature profile data show that there are two polymerization reactions occurring within the single traveling front. If there were only one reaction occurring, the second monomer would simply act as a diluent to the system and yield a monotonic decrease in velocity with an increase in the percentage unreactive monomer. The maximum temperature of the mixture is approximately a weighted average of the maximum temperature of the two separate pure systems. If the second monomer were unreactive the maximum temperature of this case would be much lower than if the second monomer were reacting but with a lower maximum temperature. Thus, from this information and the temperature profile we can conclude that a simultaneous interpenetrating polymer network was formed.

The products produced with TGDMA alone and with DGBEA alone are both transparent. However, samples from the binary fronts are opaque. However, data from transmission electron microscopy indicates that there is no phase separation. The opacity is the result of a side product from the amine curing agent.

### ***PDLCS via Frontal Polymerization***

Solutions containing an epoxy resin (EPON 862), diethylene triamine and a liquid crystal were thoroughly mixed, and polymerized via propagating front. The crosslinked polymers turned opaque when the concentration of liquid crystal was greater than 25%. This demonstrates that light scattering is occurring due to the presence of the liquid crystal. The velocity of the front decreased with increasing weight fraction of liquid crystal. The LCPDs produced in a front and in batch curing were characterized by DSC, SEM and solid state NMR. Then, the results of these LCPDs prepared by the different methods were compared.

From images taken via scanning electron microscopy (SEM), we determined that phase separated droplets of the liquid crystal only occur in the materials containing greater than 25% liquid crystal. The droplets were isotropically distributed. The sizes of the droplets produced in propagating front were approximately 1-5 microns. The droplet size decreased with increasing percentage of LC. However, the droplet density reached a minimum around 30% liquid crystal, and then around 40% liquid crystal the droplet density increases. This could be because the polymerization process does not occur in a front.

The size of the liquid crystal droplets produced in a sample that was batch cured was approximately less than 1 micron in size.

In comparison to the batch cure, fronts always produced larger drops. (Other samples were oven cured at 120 °C, 145 °C, 175 °C and 205 ° for 1 minute in 20  $\mu$  slides. All showed submicron phase separation with 30% and 40%.)

We did not expect such large droplets in the sample produced in a front. We had supposed that the rapid reaction in the front would cause very small droplets. We suppose two causes: The reaction is not as fast as in other fronts because the LC component slows the reaction. Secondly, the high temperature increases the rate of particle growth because the rate diffusion of the LC phase is increased.

**Relevance of Binary Frontal Systems** Both the IPN and PDLC work could lead to a new way to prepare large Simultaneous IPNs and PDLCs.

### **Convection in Frontal Polymerization**

Density gradients caused by thermal and solutal gradients often cause double-diffusive and/or Taylor instabilities in propagating fronts. These instabilities manifest themselves as "fingering" that can affect the front shape and velocity, and in extreme cases, destroy the front altogether. This is especially a problem with propagating fronts of polymerization when a monomer is used that produces a molten polymer, such as butyl acrylate. We have found that it is possible to suppress the fingering by rotating the tube around the long axis of the tube. With the chlorate-sulfite system and methacrylic acid polymerization system, we found that the front velocity is a function of the second power of the rotational frequency, and the front shape is parabolic. The amplitude of the deviation of the front from a planar front also exhibits the same dependence on rotational frequency.

Simple convection can extinguish fronts, especially ascending fronts. A. Taik, V. Volpert and M. Garbey of Lyon France performed a linear stability analysis of ascending thermal fronts in which liquid reactants are converted to solid product and determined a stability boundary as a function of the front velocity and initial viscosity. We have studied thermal fronts using acrylamide/bisacrylamide in DMSO. We varied the viscosity using fumed silica (Cabosil) and tested their analysis and found it worked rather well.

**Relevance** Convection is the Achilles' heel for many frontal systems. Understanding the stability criteria is essential for any possible technological application. The rotating tube method to suppress convection is a simple and effective method, which also could be applied to GRIN processes.

### **GRIN Rods**

The swelling of poly(methyl methacrylate) in its own monomer was utilized for the synthesis of cylindrical polymer pellets with the radial gradient of refractive index. Such synthesis requires the use of the polymer (PMMA) test tube. The test tube synthesis is a separate problem, which was solved using technique of the gradual immersing of the dye with monomer (two different diameter tubes, one inside another) into hot (60-70 °C) water bath.

The radial GRIN material synthesis proceeds through the following mechanism. The inner surface of the polymer test tube swells inward toward the monomer solution. The comonomers, accordingly, diffuse into polymer gel and polymerize there. The diffusion separation process (comonomers have different diffusion coefficient in the PMMA gel phase) accompanied by polymerization (comonomers have different reactivity) creates the radial gradient of the copolymer composition. Obviously, the polymerization process in the gel phase occurs in the frontal mode.

We are studying MMA - vinyl benzoate comonomer system in the 50-70 °C temperature range with different initiator (BPO) concentrations. According to the experimental conditions the GRIN synthesis can be accompanied by the polymer-copolymer phase separation that results in cloudiness of the material. Such problems can be easily eliminated using the system MMA-bromobenzene where there is no copolymerization (because bromobenzene is not a monomer here). The radial bromobenzene concentration gradient has been attained in this case due to diffusion and solidification separation processes only.

### **Relevance of GRIN Materials**

GRIN materials produce superior optical fibers, with lower transmission loss than conventional cladded materials. Also, lens arrays can be rapidly prepared.

## **Personnel Supported**

### *Graduate Student*

Mr. William Elcan, completed his M.S. December 1995

Dr. Akhtar Khan, completed his Ph.D. in August 1997

### *Technician*

Mr. Jason Willis

### *Undergraduates*

Ms. Ginger Curtis

Ms. Nicole Gill

Ms. Gina Bowden

Mr. Reade Quinton

### *Visiting Scientists*

Dr. Yuri Chekanov, Insitute of Chemical Physics, Chernogolovka, Russia

Dr. Istvan P. Nagy, Kossuth Lajos University, Debrecen Hungary

Ms. Andrea Keresztessy, Kossuth Lajos University, Debrecen Hungary

Dr. Marc Garbey, University Lyon I, Lyon France

Dr. Victor Ilyashenko (now at Boston Optical Fiber, Inc.)

## **Publications**

- (1) Khan, A. M.; Pojman, J. A. "The Use of Frontal Polymerization in Polymer Synthesis," *TRIP* **1996**, *4*, 253-257.
- (2) Pojman, J. A.; Ilyashenko, V. M.; Khan, A. M. "Free-Radical Frontal Polymerization: Self-Propagating Thermal Reaction Waves," *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 2824-2836.
- (3) Pojman, J. A.; Curtis, G.; Ilyashenko, V. M. "Frontal Polymerization in Solution," *J. Am. Chem. Soc.* **1996**, *115*, 3783-3784.



- (4) Pojman, J. A.; Willis, J. R.; Khan, A. M.; West, W. W., "The True Molecular Weight Distributions of Acrylate Polymers formed in Propagating Fronts," *J. Polym. Sci. Part A: Polym Chem.* **1996**, *34*, 991-995.
- (5) Nagy, I. P.; Pojman, J. A., "Suppressing Convective Instabilities in Propagating Fronts by Tube Rotation," *J. Phys. Chem.* **1996**, *100*, 3299-3304.
- (6) Nagy, I. P.; Sike, L.; Pojman, J. A., "Thermochromic Composites and Propagating Polymerization Fronts," *Adv. Mat.* **1995**, *7*, 1038-1040.
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- (7) Pojman, J. A.; Curtis, G.; Ilyashenko, V. M. "Frontal Polymerization in Solution," *J. Am. Chem. Soc.* **1996**, *115*, 3783-3784.
- (8) Pojman, J. A.; Elcan, W.; Khan, A. M.; Mathias, L. "Binary Polymerization Fronts: A New Method to Produce Simultaneous Interpenetrating Polymer Networks (SINs)," *J. Polym. Sci. Part A: Polym Chem.* **1997**, *35*, 227-230.
- (9) Bowden, G.; Garbey, M.; Ilyashenko, V. M.; Pojman, J. A.; Solovyov, S.; Taik, A.; Volpert, V. "The Effect of Convection on a Propagating Front with a Solid Product: Comparison of Theory and Experiments," *J. Phys. Chem. B* **1997**, *101*, 678-686.
- (10) Pojman, J.; Fortenberry, D.; Ilyashenko, V. "Frontal Polymerization as an Analog of SHS," *Int. J. SHS* **1997**, *6*, 355-376.
- (11) Chekanov, Y.; Arrington, D.; Brust, G.; Pojman, J. A. "Frontal Curing of Epoxy Resin: Comparison of Mechanical and Thermal Properties to Batch Cured Materials," *J. Appl. Polym. Sci.* **1997**, *66*, 1209-1216.

### **Interactions/Transitions:**

#### **a) Presentations at Meetings**

##### **1. National Meetings**

"Spin Modes and Pulsations in Propagating Fronts of Addition Polymerization"

John A. Pojman\*, Victor Ilyashenko and Akhtar Khan, Dynamics Days, Houston, TX January 5, 1995

"Instabilities in Propagating Fronts of Polymerization", Workshop on Instabilities and Propagating Fronts, University Lyon I, Lyon France, April 27, 1995

"Binary Polymerization Fronts: A New Method to Produce Simultaneous Interpenetrating Polymer Networks (SINs)", InterSociety Polymer Meeting, October 7 -10, Baltimore, MD William Elcan, Akhtar M. Khan, Lon Mathias and John A. Pojman\*, 1995

"Frontal Polymerization: From Dynamics to Materials," invited presentation at 28th Congres National D'Analyse Numerique, La Londe-Les Maures, France, May 29, 1996

"Applications of Frontal Polymerization to Materials Synthesis," NSF Workshop on Materials Chemistry, October 17, Philadelphia, PA, 1996

"Frontal Polymerization: *Quo Vadis?*," John A. Pojman, American Chemistry Society National Meeting, New Orleans, March 25, 1996

"Periodic Modes of Frontal Polymerization," Victor M. Ilyashenko and John A. Pojman, American Chemical Society National Meeting, New Orleans, March 25

"Frontal Polymerization of n-Butyl Acrylate," Akhtar M. Khan and John A. Pojman, American Chemical Society National Meeting, New Orleans, March 26

"Frontal Polymerization of in Solution," Gina Bowden, Ginger Curtis, Victor Ilyashenko and John A. Pojman, American Chemical Society National Meeting, New Orleans, March 26, 1996

"Frontal Curing of Epoxies," Gina Bowden and John A. Pojman, American Chemical Society National Meeting, New Orleans, March 26, 1996

"Binary Frontal Polymerization: A New Method to Produce Simultaneous Interpenetrating Polymer Networks (SINs)" John A. Pojman\*, William Elcan, Akhtar M. Khan, Chris Simmons and Lon Mathias, American Chemical Society National Meeting, Orlando, August 26, 1996

"Isothermal Frontal Polymerization," Victor Ilyashenko and John A. Pojman, American Chemical Society National Meeting, Orlando, August 26, 1996

"Polymer Dispersed Liquid Crystal (PDLC) Materials Produced via Frontal Epoxy Curing," John Pojman\*, Nicole Gill<sup>a</sup>, and Jason Willis<sup>a</sup>, Joe B. Whitehead American Chemical Society National Meeting, Orlando, August 26, 1996

"Reactor Design and Performance for the Study of Frontal Polymerization," John A. Pojman\* and Akhtar M. Khan, American Chemical Society National Meeting, Orlando, August 26, 1996

"The Effect of Convection on Propagation Polymerization Fronts," John A. Pojman, Oscillations and Dynamic Instabilities in Chemistry (Gordon Conference) July 14, New Port, RI, 1997

"Frontal Curing of Epoxies," Yuri Chekanov and John A. Pojman, ACS National Meeting, April 14, San Francisco, 1997.

"Frontal Polymerization in Microgravity," John A. Pojman, A. Khan and Lon Mathias, ACS National Meeting, April 14, San Francisco, 1997.

"Solvent-less Processing by Frontal Polymerization," John A. Pojman, Chris Simmons, L. Lee Lewis, Victor Ilyashenko, ACS National Meeting, September 8 - 11, Las Vegas, 1997

"Frontal Dispersion Polymerization," John A. Pojman, Grady Gunn, Chilibra Patterson, Chris Simmons, ACS National Meeting, September 8 - 11, Las Vegas 1997

## 2. Regional Meetings

ACS SE/SW Regional Meeting in Memphis November 28 - December 1 1995

**AN INVESTIGATION OF BINARY POLYMERIZATION FRONTS EMPLOYING TWO DIFFERENT AND NON-INTERFERING POLYMERIZATION MECHANISMS.**

William H. Elcan\* and Dr. John A. Pojman, Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, MS 39406.

**SUPPRESSION OF DOUBLE-DIFFUSIVE AND TAYLOR INSTABILITIES IN PROPAGATING FRONTS BY TUBE ROTATION. John A. Pojman,**

Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, MS 39406 and Istvan Nagy, Department of Physical Chemistry, Kossuth Lajos University, H-4010 Debrecen, pf. 7 Hungary

**PROPAGATING FRONTS OF ACRYLAMIDE DILUTED WITH BARIUM CARBONATE** Ginger C. Curtis\*, Victor M. Ilyashenko and John A. Pojman, Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, MS 39406.

**ANALYSIS OF FRONTAL FREE-RADICAL POLYMERIZATION IN VARIOUS SOLID MONOMERS**

Dionne I. Fortenberry\* and John A. Pojman, Department of Chemistry and Biochemistry, University of Southern Mississippi., Hattiesburg, MS 39406

**Characterization of Liquid Crystal Polymer Dispersions (LCPD) Produced in Propagating Fronts of Epoxy Curing,** Nicole Gill\*, Joe Whitehead, John A. Pojman, Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, MS 39406

**Convection in Ascending Fronts of Epoxy Curing: Comparison of Experiment to Linear Stability Analysis**

Gina Bowden and John A. Pojman, Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, MS, 39406.

3. State Meetings

Mississippi Academy of Sciences, Biloxi, MS February 17- 18

**Functionally Gradient and Phase-Separated Polymers Produced From Propagating Polymerization Fronts.**

William H. Elcan\* and John A. Pojman, Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, MS, 39406.

**A Study of Self-Propagating Polymerization Fronts in Commercial Epoxy Systems**

Reade A. Quinton\* and John Pojman, Dept. of Chemistry, University of Southern Miss., Hattiesburg, MS 39406

### **Self-Propagating Frontal Polymerization: Experimental Technique and Reactor Design and Performance**

Akhtar M. Khan\* and John A. Pojman, Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, MS 39406

### **Factors Affecting Propagating Fronts of Addition Polymerization: Conversion and Molecular Weight Distribution**

Jason Willis\* and John A. Pojman, Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, MS 39406-5043

"Frontal Curing of Epoxies," Gina Bowden and John A. Pojman, Mississippi Academy of Sciences, February 1996

"Convective Instabilities in Frontal Polymerization," Chris Simmons and John A. Pojman, Mississippi Academy of Sciences Annual Meeting, February 21, Biloxi, MS 1997.

### **Transition Items:**

- (1) John A. Pojman, University of Southern Mississippi
- (2)
  - a) dye gradient polymeric materials produced by thermal frontal polymerization
  - b) crosslink-gradient polymeric materials
- (3) (AFOSR/NL, Dr. Charles Lee, 202-767-5022)
- (4)
  - a) for laser limiting optics
  - b) for proof of concept for producing functionally gradient materials frontally

### **New Discoveries**

- a method to suppress convection in frontal polymerization
- developed new method to prepare simultaneous IPNs
- discovered the first frontal polymerization in solution
- discovered a method to produce functionally gradient materials, e.g., with gradients of dye concentration or crosslink density

### **Honors/Awards**

PI was tenured and promoted to Full Professor.